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14. ABSTRACT <p>Computed ultrafast, (attosecond), electron migration in LiH where the axis of the molecule is along the z direction. The computation demonstrates the control that can be applied via the polarization of the pump laser. Shown is a three dimensional plot of the motion of the electronic dipole of LiH. Shown are the x and z components of the dipole as time unfolds. The pump pulse is short, about 1 fs. (Left). A pump pulse polarized in the z direction. The dipole oscillates along z and there is no component along the x axis. (Right). A pump polarized along the xz direction. The longest period is a rotation of the dipole about the axis of the molecule with a period of about 4 fs. This period is indicated.</p>					
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Chemical Behavior Under Extreme Conditions

A Proposal submitted to

The Air Force Office of Scientific Research

Directorate of Chemistry and Life Sciences

By

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January 11, 2008

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Background

I submitted to AFOSR a four-year proposal of theoretical research on matter of high energy and material density in January 2005. The proposal was initially approved for funding for one year with an option for an extension for a second year. This option has been granted. Then I was invited to submit a new two year proposal covering the same general topics. The following report is the final performance report for the new, two-year grant.

The subjects of the four-year proposal of 2005 were special aspects that are due to high material density. These are repeated herein:

- The characterization of 'pressure' and the equation of state of systems in extreme disequilibrium with strong internal forces.

Excellent progress is reported in four papers in the open scientific literature. The referee reports on these papers are amongst the very best that I have received in my entire professional life.

- Are genuine termolecular (and higher order?) chemical processes made possible by the high density and, in general, what new chemistry is possible at high pressure ?

We refer to our new proposal on the coupling of chemistry and hypersonic flight for more details. We further believe that the brand new computational methodology that we discuss therein will allow us to make further and significant progress.

- The role of a hot and dense environment in activating/deactivating polyatomic species

We have detailed results for water molecules. Publication has been delayed by experiments seeking to match the theory. This is now completed and ready for publication. Some theoretical results are summarized in an appendix.

- The electronic excitation that results from close-in collisions

We report below that it should be possible to steer electronic motion and to thereby control the forces on the nuclei. Several papers have already been published.

We have what we consider promising preliminary work on electronic excitation and this work has already generated offers from several leading experimental groups for work on

the experimental manifestations. There are reasons for suggesting that this work could have wide implications all the way to bioelectronic functionalities.

The original four-year proposal has a detailed discussion of the four points including references etc. The work of the first two years was covered in the previous final report. So the discussion below puts the emphasis on the pure electron dynamics because our very recent work led to some worthwhile progress.

Steered Ultrafast Quantum Dynamics of Electrons

Graphic abstract:

Computed ultrafast, (attosecond), electron migration in LiH where the axis of the molecule is along the z direction. The computation demonstrates the control that can be applied via the polarization of the pump laser. Shown is a three dimensional plot of the motion of the electronic dipole of LiH. Shown are the x and z components of the dipole as time unfolds. The pump pulse is short, about 1 fs. (Left). A pump pulse polarized in the z direction. The dipole oscillates along z and there is no component along the x axis. (Right). A pump polarized along the xz direction. The longest period is a rotation of the dipole about the axis of the molecule with a period of about 4 fs. This period is indicated.

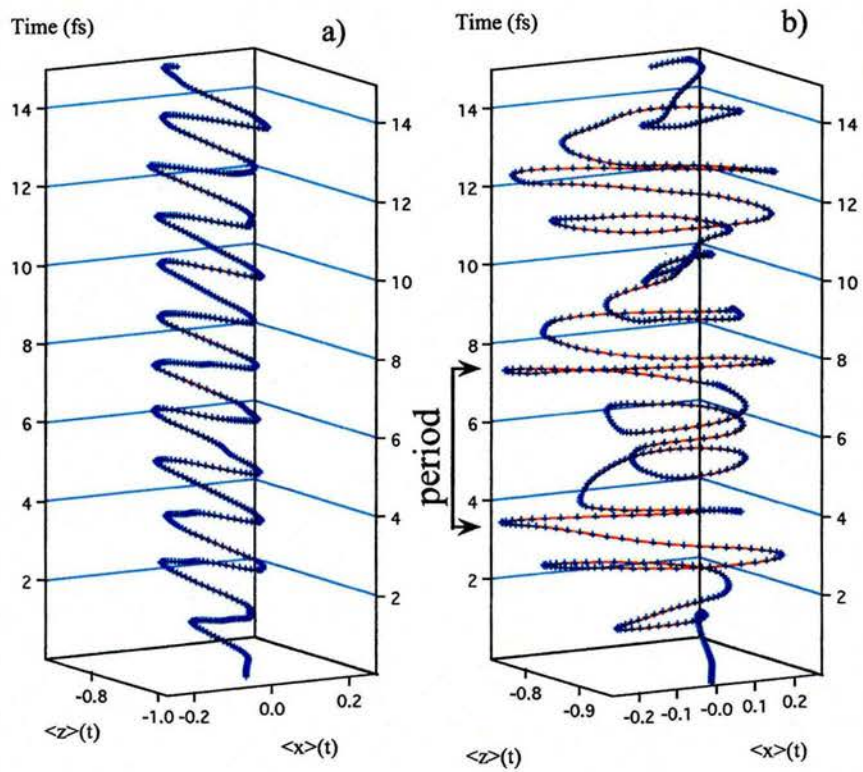


Figure 5 : lg12z and lg12xz

technical abstract

A time dependent multi-configuration method with a large electronic basis set is used to compute the response of all the electrons of LiH to a few-cycle intense pump field followed by a probe pulse. The ultrashort pump pulse excites a coherent superposition of stationary electronic states and by changing the pump parameters such as intensity, duration, polarization and phase of carrier frequency one can steer the motion of the electrons. Particular attention is given to the control provided by the polarization and by the phase. For example, a change in polarization is used to select an electronic wave packet that is rotating in a plane perpendicular to the bond or rotation in a plane containing the bond. The electronic wave packet can be probed by a delayed second pulse. This delayed probe pulse is also included in the Hamiltonian with the result that the frequency dispersed probe spectrum can be computed and displayed as a 2 dimensional plot. Lastly we showed how to controll the force on the nuclei through the variation of the phase between the amplitude and the carrier of the laser few cycle pulse.

Motivation for this work

The fundamental theory for chemistry is that of electronic structure. Chemical theory blossomed when quantum mechanics provided the means to understand the energetics and dynamics of electronic motion. Yet the time scale for chemistry is not that for the movement of electrons. The reason is that the central subject of chemistry is the chemical change. An elementary change occurs when atoms in a molecule change their specific arrangement. The time scale of chemistry is therefore the time scale for the motion of atoms ^[1-3]. The picture is that the electrons instantly adjust to the current position of the nuclei so that the equilibrium arrangement of the bonded atoms is determined as a minimum of the electronic energy. The forces that set the atoms in motion are determined by the changes in this energy. If this view holds then there is no electronic time scale that is relevant to Chemistry. During a chemical rearrangement the motion of the atoms can be accompanied by a reorganization of the electronic structure and recent experimental progress allows for probing this change ^[4] in real time. However, it is the motion of the nuclei that sets the time scale because the electronic reorganization exactly tracks the shifts in the positions of the nuclei. As the heavier nuclei move the light electrons immediately adapt and so the electrons cannot be displaced from a stationary state*.

Attosecond ($1 \text{ as} = 10^{-18} \text{ sec}$) laser pulses are becoming available ^[8-13]. The proposed research is to ask if using such short pulses it is possible to access and probe non stationary electronic states and, furthermore if such non stationary electronic states are relevant to biophysical chemistry. In particular we ask if one can unravel some of the current mysteries in biological oxidation-reduction processes, in ultrafast signal transduction upon optical excitation as in vision and in other, seemingly action at a distance, distal biological processes ^[14]. However, an essential preliminary stage is to directly demonstrate experimentally and to provide theoretical understanding for non stationary electronic processing in model systems. Only then can we securely demonstrate the relevance of an electronic time scale for biological signal transduction.

* It is nowadays well understood that this is an approximation that will fail at a, so called, conical intersection [5-7]. Even then, the failure requires the nuclei to move and the time scale remains that of the motion of the nuclei.

In the past year we have focused on a particular molecule, LiH, for which exact numerical computations can be performed even when including both the pump and the probe pulses. In the coming year we propose to further develop this approach to pump-probe with special reference to the new experimental capabilities at the MPQ and with special reference to the progress in the junior research groups of Reinhard Kienberger, Matthias Lezius and Jens Rauschenberger where ultrashort pulses with photon energy in the 5-10 eV range are being produced. We are in close attention with these developments.

Several papers reporting on this new direction have already been published as is reported in below.

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Publications during the period of this proposal

The Entropy of a Single Large Finite System Undergoing Both Heat and Work Transfer, A. Gross and R. D. Levine, *Mol. Phys.* 105, 419 (2007).

Inter- and intramolecular level logic devices, F. Remacle and R. D. Levine in *Information Technology*, R. Waser (Ed.), Wiley (2007).

The emergence of a coupled quantum dot array in a doped Silicon nanowire gated by ultrahigh density top gate electrodes, Ke Xu, Jonathan E. Green, J. R. Heath, F. Remacle and R. D. Levine, *J. Phys. Chem.* (2007).

Probing Ultrafast Purely Electronic Charge Migration in Small Peptides, F. Remacle and R. D. Levine, *Zeit. Phys. Chem.*, 221, 647 (2007).

Ultrafast Purely Electronic Reorganization in Lithium Hydride, F. Remacle, Reinhard Keinberger, Ferenc Krausz and R. D. Levine, *Chem. Phys.* 338, 342 (2007).

Transcending Binary Logic by Gating Three Coupled Quantum Dots, Michael Klein, S. Rogge, F. Remacle and R. D. Levine, *Nano Letters* 7, 2795 (2007)..

Steered Ultrafast Quantum Dynamics of Electrons in LiH, F. Remacle, M. Nest and R. D. Levine, *Phys. Rev. Lett.* 99, 183902 (2007).

Ultrafast Vibrational Spectroscopy and Relaxation in Polyatomic Molecules: Potential for Molecular Parallel Computing, E.A. Torres, K.L. Kompa, F. Remacle and R.D. Levine, *Chem. Phys.* 347, 531 (2008).

Pump and Probe Ultrafast Electron Dynamics in LiH: a Computational Study, M. Nest, F. Remacle, and R. D. Levine, *New J. Phys.* 10 (2008).

All optical full adder based on intramolecular electronic energy transfer in the rhodamine-azulene bichromophoric system, O. Kuznetz, H. Salman, Y. Eichen, F. Remacle, R. D. Levine and S. Speiser: *J. Phys. Chem. C* 112, 15880 (2008).

Principles of design of a set-reset finite state logic nanomachine, M. Klein, R. D. Levine and F. Remacle: *J. Appl. Phys.* 104 (2008).

A cumulative list of publications in the area of chemistry under extreme conditions is available upon request.

Interactions/Transitions:

The work carried out under the auspices of this proposal has been reported at conferences and seminars, most recently as an invited talk to be presented the 2009 National Meeting of the American Chemical Society and as the first Bernstein Memorial Lecture at the University of Wisconsin in April 2009.

New discoveries, inventions, or patent disclosures. (If none, report None.)

None

Honors/Awards:

Two special issues of journals dedicated to R. D. Levine have been published in 2008. *The Israel Journal of Chemistry*, edited by R. N. Zare and I. Schechter and the 2008 issues 2-4 of *Molecular Physics* edited by S. Kais and N. C. Handy.

Appendix: On the shattering of water clusters

The work discussed is based on the idea of a cluster impact where a cold cluster hits a rigid surface. Before the collision with the surface, the direction of the velocity of all the components of the clusters is essentially the same. Although the velocity of the center of mass is high, the relative kinetic energies of the components of the cold cluster before the collision are very low. As a result of the impact with the surface, the front layers of the clusters changed their direction of velocity while the rest of the cluster is still moving forward. The result is that within the cluster its constituents collide with very high relative kinetic energy. Thereby cluster impact provides a new regime of dynamics, where the energy exchange process is thermal (due to collisions) but it occurs on a very short time scale (comparable to vibrational periods). Hitherto this was only possible by photo activation. Ordinary chemistry occurs in a regime where collisions are fast on the rotational time scale but slow on the vibrational one. A new regime-**thermally-induced femto-chemistry**-is made available for study. The high material density arises from the compression of the cluster upon impact.

After not many collisions the hot and dense cluster shatters. In the 2005 proposal we drew special attention to water clusters. The work of the past year emphasized this subject. The work is currently being prepared for publication in cooperation with the two experimental groups.

Initially, the comparison between experiment and theory was rather frustrating. It was then realized that unlike van der Waals clusters, impact of water clusters leave a significant deposit of water on the surface. Therefore the theory has to take into account that the cluster collides with a water covered surface. This was not quite simple and took quite some time but once it was implemented the agreement between the theory and experiment is much better. The theory that we report on below is based on the maximum entropy formalism that has been extensively applied before to cluster impact. In view of its success we plan to report next year on classical trajectory simulations of the same system.

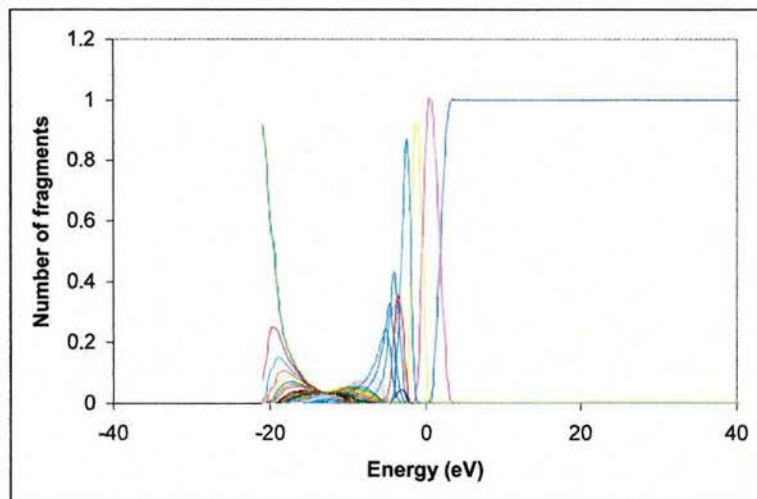
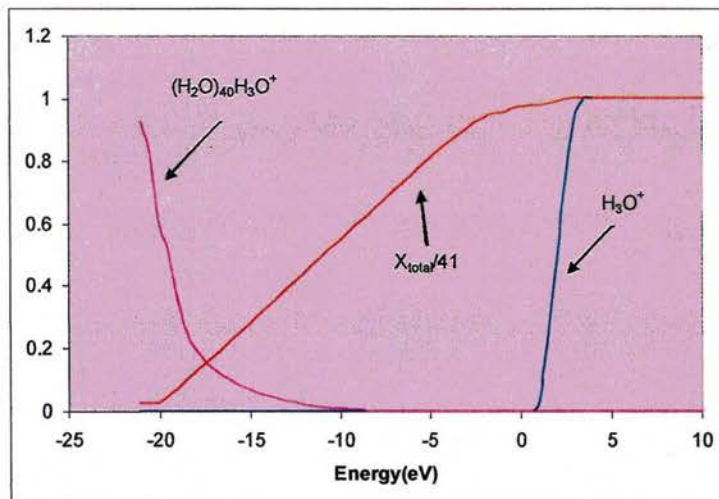


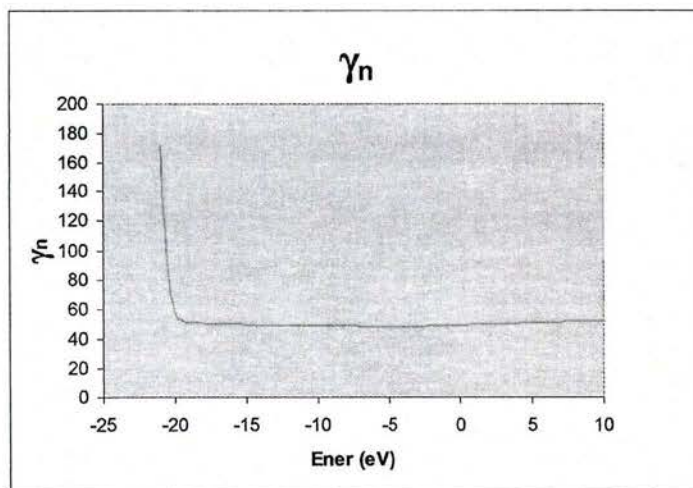
Figure 1 shows the computed results when a cluster of 41 water molecules, $(\text{H}_2\text{O})_{40}\text{H}_3\text{O}^+$ impacts a surface spot covered by 400 water molecules, as a function of the total energy of the system. Shown is the disappearance of the parent ion followed by a range of energies in which many fragments are produced. Then, as the energy is increased further it is mostly $(\text{H}_2\text{O})_n\text{H}_3\text{O}^+$ ions, $n=3,2,1,0$. Finally only the unsolvated H_3O^+ ion remains. What is seen in the experiment and also in figure 1 is the intermediate regime where there are hardly any ions. This is the energy range where the solvated ion remains within the water coverage on the surface.

Figure 2 is an alternative view of the results shown in figure 1

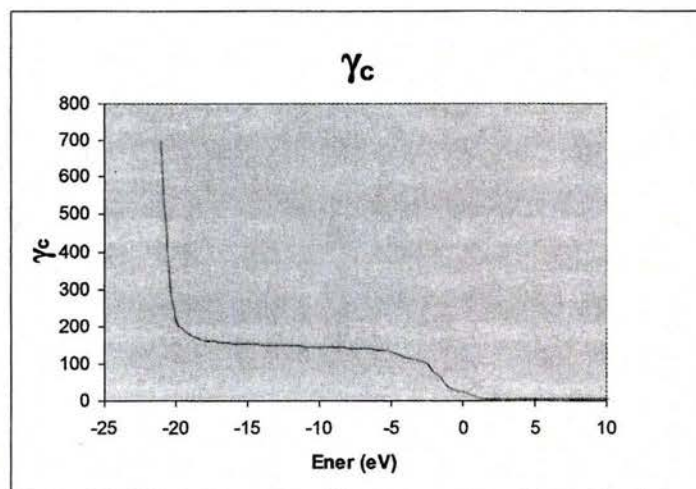


It shows the decline of the parent ion and the much later rise of the unsolvated ion. X is the total number of fragments, charged or not. So $X/41$ can vary from $1/41$ to 1. The value of 1 is possible only when the parent cluster is fully fragmented into individual water molecules. The results show that this is what does happen.

Figures 3 and 4 are of interest to the theorists. We proposed to show that the cluster undergoes a phase transition. These figures provide the proof. In fact, even more so than expected. A phase transition is when a chemical potential is a discontinuous function of the temperature (here, the collision energy). Figure 3 shows this transition for the chemical potential of water molecules. At the very onset of the extensive fragmentation, compare figures 3 and 2, the discontinuity is self evident.



The plot of the chemical potential of the positive charge, shown below, exhibits TWO discontinuities. One is at the expected energy as in figure 3. But there is another discontinuity near the total energy of zero.



Zero is the energy where the cluster is fully fragmented into water molecules at rest. The transition is from a solvated to a bare H_3O^+ ion!